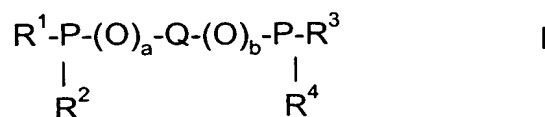


We claim:

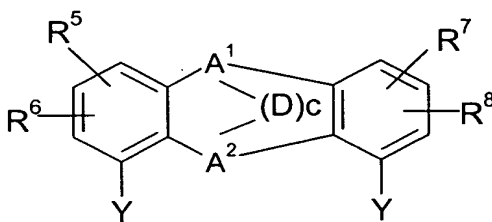
1. A process for the continuous preparation of aldehydes having from 5 to 21 carbon atoms by isomerizing hydroformylation in the homogeneous phase of olefin compositions having from 4 to 20 carbon atoms and comprising α -olefins and olefins having internal double bonds by means of synthesis gas in the presence of a homogeneous rhodium catalyst complexed with an oxygen- and/or nitrogen-containing organophosphorus ligand and free ligand at elevated temperature and elevated pressure in a multistage reaction system comprising at least two reaction zones, wherein the olefin composition is firstly reacted with synthesis gas having a CO/H₂ molar ratio of from 4:1 to 1:2 at a total pressure of from 10 to 40 bar in a group of one or more first reaction zones to a conversion of the α -olefins of from 40 to 95% and the hydroformylation mixture from this group of one or more first reaction zones is reacted with synthesis gas having a CO/H₂ molar ratio of from 1:4 to 1:1000 at a total pressure of from 5 to 30 bar in a group of one or more downstream reaction zones, where the total pressure in the one or more downstream reaction zones is in each case from 1 to (T1-Tf) bar lower than in the preceding reaction zone, where T1 is the total pressure in the preceding reaction zone and Tf is the total pressure in the reaction zone downstream of the one or more first reaction zones, with the proviso that the difference T1-Tf is greater than 1 bar, and the CO partial pressure in the one or more downstream reaction zones is in each case lower than in the reaction zone preceding this reaction zone.
2. A process as claimed in claim 1, wherein a CO/H₂ molar ratio of from 3:2 to 2:3 is set in the one or more first reaction zones and a CO/H₂ molar ratio of from 1:9 to 1:100 is set in the one or more downstream reaction zones.
3. A process as claimed in claim 1 or 2 which is carried out in two reaction zones.
4. A process as claimed in any of claims 1 to 3, wherein hydrogen-containing offgases from aldehyde and enal hydrogenation processes is used to set the CO/H₂ molar ratio in the one or more reaction zones downstream of the first reaction zones.
5. A process as claimed in any of claims 1 to 4, wherein the homogeneous hydroformylation catalyst used is a complex of rhodium with a phosphoramidite ligand of the formula I

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where

5 Q is a bridging group of the formula



where

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A¹ and A² are each, independently of one another, O, S, SiR^aR^b, NR^c or CR^dR^e,
where

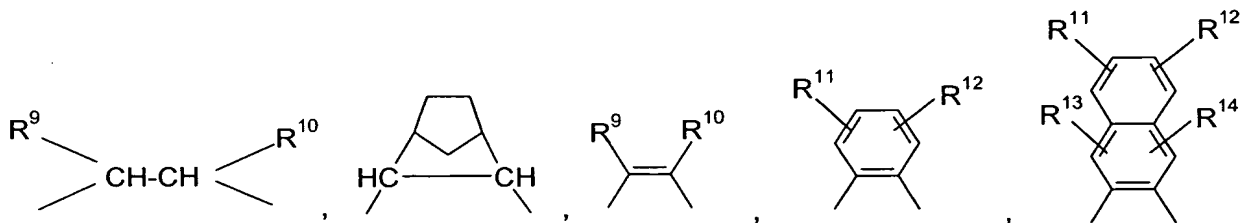
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R^a, R^b and R^c are each, independently of one another, hydrogen, alkyl,
cycloalkyl, heterocycloalkyl, aryl or hetaryl,

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R^d and R^e are each, independently of one another, hydrogen, alkyl, cycloalkyl,
heterocycloalkyl, aryl or hetaryl or together with the carbon atom to which
they are bound form a cycloalkylidene group having from 4 to 12 carbon
atoms or the group R^d together with a further group R^d or the group R^e
together with a further group R^e forms an intramolecular bridging group D,

D is a divalent bridging group selected from among the groups



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where

R^9 and R^{10} are each, independently of one another, hydrogen, alkyl, cycloalkyl, aryl, halogen, trifluoromethyl, carboxyl, carboxylate or cyano or are joined to one another to form a C_3 - to C_4 -alkylene bridge,

5 R^{11} , R^{12} , R^{13} and R^{14} are each, independently of one another, hydrogen, alkyl, cycloalkyl, aryl, halogen, trifluoromethyl, COOH, carboxylate, cyano, alkoxy, SO_3H , sulfonate, NE^1E^2 , alkylene- $NE^1E^2E^{3+}X^-$, acyl or nitro,

c is 0 or 1,

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Y is a chemical bond,

15

R^5 , R^6 , R^7 and R^8 are each, independently of one another, hydrogen, alkyl, cycloalkyl, heterocycloalkyl, aryl, hetaryl, $COOR^f$, COO^-M^+ , SO_3R^f , $SO_3^-M^+$, NE^1E^2 , $NE^1E^2E^{3+}X^-$, alkylene- $NE^1E^2E^{3+}X^-$, OR^f , SR^f , $(CHR^9CH_2O)_xR^f$, $(CH_2N(E^1))_xR^f$, $(CH_2CH_2N(E^1))_xR^f$, halogen, trifluoromethyl, nitro, acyl or cyano,

where

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R^f , E^1 , E^2 and E^3 are identical or different radicals selected from among hydrogen, alkyl, cycloalkyl and aryl,

R^9 is hydrogen, methyl or ethyl,

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M^+ is a cation,

X^- is an anion and

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x is an integer from 1 to 120,

or

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R^5 and/or R^7 together with two adjacent carbon atoms of the benzene ring to which they are bound form a fused ring system having 1, 2 or 3 further rings,

a and b are each, independently of one another, 0 or 1,

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P is a phosphorus atom,

and

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R^1 , R^2 , R^3 , R^4 are each, independently of one another, hetaryl, hetaryloxy, alkyl, alkoxy, aryl, aryloxy, cycloalkyl, cycloalkoxy, heterocycloalkyl,

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heterocycloalkoxy or an NE^1E^2 group, with the proviso that R^1 and R^3 are bound via the nitrogen atom of pyrrole groups bound to the phosphorus atom P or R^1 together with R^2 and/or R^3 together with R^4 form a divalent group E which contains at least one pyrrole group bound via the pyrrole nitrogen to the phosphorus atom P and has the formula

Py-I-W

where

Py is a pyrrole group,

I is a chemical bond or O, S, SiR^aR^b , NR^c or CR^hR^i ,

W is cycloalkyl, cycloalkoxy, aryl, aryloxy, hetaryl or hetaryloxy,

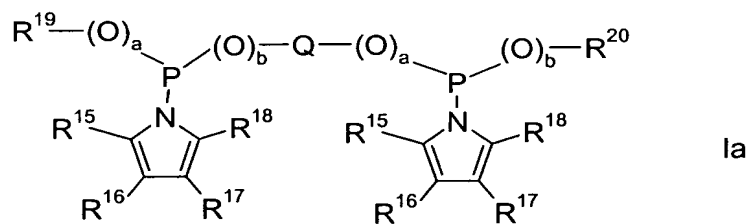
and

R^h and R^i are each, independently of one another, hydrogen, alkyl, cycloalkyl, heterocycloalkyl, aryl or hetaryl,

or form a bispyrrole group which is bound via the nitrogen atoms to the phosphorus atom P and has the formula

Py-I-Py.

6. A process as claimed in any of claims 1 to 5, wherein the homogeneous hydroformylation catalyst used is a complex of rhodium with a phosphoramidite ligand of the formula Ia



where

R^{15} , R^{16} , R^{17} and R^{18} are each, independently of one another, hydrogen, alkyl, cycloalkyl, heterocycloalkyl, aryl, hetaryl, $\text{W}'\text{COOR}^k$, $\text{W}'\text{COO}^-\text{M}^+$, $\text{W}'(\text{SO}_3)\text{R}^k$, $\text{W}'(\text{SO}_3)^-\text{M}^+$, $\text{W}'\text{PO}_3(\text{R}^k)(\text{R}^l)$, $\text{W}'(\text{PO}_3)_2(\text{M}^+)_2$, $\text{W}'\text{NE}^4\text{E}^5$,

$W'(NE^4E^5E^6)^+X^-$, $W'OR^k$, $W'SR^k$, $(CHR^lCH_2O)_yR^k$, $(CH_2NE^4)_yR^k$, $(CH_2CH_2NE^4)_yR^k$, halogen, trifluoromethyl, nitro, acyl or cyano,

where

5

W' is a single bond, a heteroatom or a divalent bridging group having from 1 to 20 bridge atoms,

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R^k , E^4 , E^5 , E^6 are identical or different radicals selected from among hydrogen, alkyl, cycloalkyl and aryl,

R^l is hydrogen, methyl or ethyl,

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M^+ is a cation equivalent,

X^- is an anion equivalent and

y is an integer from 1 to 240,

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where two adjacent radicals R^{15} , R^{16} , R^{17} and R^{18} together with the carbon atoms of the pyrrole ring to which they are bound may also form a fused ring system having 1, 2 or 3 further rings,

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with the proviso that at least one of the radicals R^{15} , R^{16} , R^{17} and R^{18} is not hydrogen and R^{19} and R^{20} are not linked to one another,

R^{19} and R^{20} are each, independently of one another, cycloalkyl, heterocycloalkyl, aryl or hetaryl,

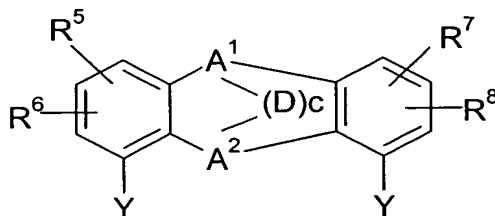
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a and b are each, independently of one another, 0 or 1,

P is a phosphorus atom,

Q is a bridging group of the formula

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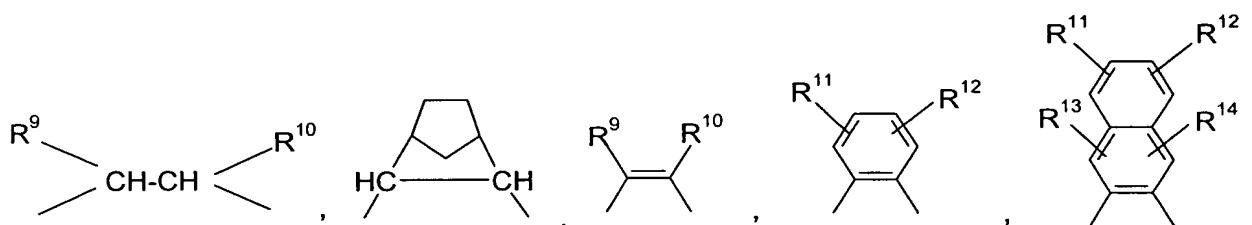
where

A^1 and A^2 are each, independently of one another, O, S, SiR^aR^b , NR^c or CR^dR^e ,
where

R^a , R^b and R^c are each, independently of one another, hydrogen, alkyl,
cycloalkyl, heterocycloalkyl, aryl or hetaryl,

R^d and R^e are each, independently of one another, hydrogen, alkyl, cycloalkyl,
heterocycloalkyl, aryl or hetaryl or together with the carbon atom to which
they are bound form a cycloalkylidene group having from 4 to 12 carbon
atoms or the group R^d together with a further group R^d or the group R^e
together with a further group R^e forms an intramolecular bridging group D,

D is a divalent bridging group selected from among the groups



where

R^9 and R^{10} are each, independently of one another, hydrogen, alkyl, cycloalkyl,
aryl, halogen, trifluoromethyl, carboxyl, carboxylate or cyano or are joined
to one another to form a C_3 - to C_4 -alkylene bridge,

R^{11} , R^{12} , R^{13} and R^{14} are each, independently of one another, hydrogen, alkyl,
cycloalkyl, aryl, halogen, trifluoromethyl, COOH, carboxylate, cyano,
alkoxy, SO_3H , sulfonate, NE^1E^2 , alkylene- $NE^1E^2E^3X^-$, acyl or nitro,

c is 0 or 1,

R^5 , R^6 , R^7 and R^8 are each, independently of one another, hydrogen, alkyl,
cycloalkyl, heterocycloalkyl, aryl, hetaryl, $COOR^f$, COO^-M^+ , SO_3R^f , $SO_3^-M^+$,
 NE^1E^2 , $NE^1E^2E^3X^-$, alkylene- $NE^1E^2E^3X^-$, OR^f , SR^f , $(CHR^9CH_2O)_xR^f$,
 $(CH_2N(E^1))_xR^f$, $(CH_2CH_2N(E^1))_xR^f$, halogen, trifluoromethyl, nitro, acyl or
cyano,

where

R^f , E^1 , E^2 and E^3 are identical or different radicals selected from among
hydrogen, alkyl, cycloalkyl and aryl,

5 R^9 is hydrogen, methyl or ethyl,

M^+ is a cation,

X^- is an anion and

x is an integer from 1 to 120,

10 or

R^5 and/or R^7 together with two adjacent carbon atoms of the benzene ring to which they are bound form a fused ring system having 1, 2 or 3 further rings.

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7. A process as claimed in claim 1, wherein the olefin composition used is a raffinate II.

Continuous preparation of aldehydes

Abstract

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Process for the continuous preparation of aldehydes having from 5 to 21 carbon atoms by isomerizing hydroformylation in the homogeneous phase of olefin compositions having from 4 to 20 carbon atoms and comprising α -olefins and olefins having internal double bonds by means of synthesis gas in the presence of a homogeneous rhodium catalyst complexed with an oxygen- and/or nitrogen-containing organophosphorus ligand and free ligand at elevated temperature and elevated pressure in a multistage reaction system comprising at least two reaction zones, in which the olefin composition is firstly reacted with synthesis gas having a CO/H₂ molar ratio of from 4:1 to 1:2 at a total pressure of from 10 to 40 bar in a group of one or more first reaction zones to a conversion of the α -olefins of from 40 to 95% and the hydroformylation mixture from this group of one or more first reaction zones is reacted with synthesis gas having a CO/H₂ molar ratio of from 1:4 to 1:1000 at a total pressure of from 5 to 30 bar in a group of one or more downstream reaction zones, where the total pressure in the one or more downstream reaction zones is in each case from 1 to (T1-Tf) bar lower than in the preceding reaction zone, where T1 is the total pressure in the preceding reaction zone and Tf is the total pressure in the reaction zone downstream of the one or more first reaction zones, with the proviso that the difference T1-Tf is greater than 1 bar, and the CO partial pressure in the one or more downstream reaction zones is in each case lower than in the reaction zone preceding this reaction zone.

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